# Bulk spin polarization of magnetite from spin-resolved hard x-ray photoelectron spectroscopy

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There is broad consensus that magnetite (Fe<sub>3</sub>O<sub>4</sub>) is a promising material for spintronics applications due to its high degree of spin polarization at the Fermi level. However, previous attempts to measure the spin polarization by spin-resolved photoemission spectroscopy have been hampered by the use of *low photon energies* resulting in high surface sensitivity. The surfaces of magnetite, though, tend to reconstruct due to their polar nature, and thus their magnetic and electronic properties may strongly deviate from each other and from the bulk, dependent on their orientation and specific preparation. In this study, we determine the intrinsic—i.e., bulk—spin polarization of magnetite by spin-resolved photoelectron spectroscopy on (111)-oriented thin films, epitaxially grown on ZnO(0001), with *hard x-rays*, making it a truly bulk-sensitive probe. This becomes possible by using a novel, specially adapted momentum microscope, featuring time-of-flight energy recording and an imaging spin-filter.

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## I. INTRODUCTION

Ferrimagnetic magnetite (Fe<sub>3</sub>O<sub>4</sub>) has been a focus of research for many years due to its half-metallic properties, making it an interesting candidate material for spin-electrodes in spintronic devices such as, e.g., a Datta-Das spin transistor [1,2], all the more as magnetite has a very high Curie temperature of 858 K [3].

The half-metallic properties can be understood from its inverse-spinel structure (space group  $Fd\bar{3}m$ ) with tetrahedrally (Fe<sub>A</sub>) and octahedrally (Fe<sub>B</sub>) coordinated iron sublattices. While the Fe<sub>A</sub> ions are in the oxidation state 3+, Fe<sup>2+</sup> and Fe<sup>3+</sup> ions are randomly distributed over the Fe<sub>B</sub> sublattice [4]. Since there are twice as many *B* as *A* sites and the spins of the two sublattices couple antiferromagnetically, the remaining itinerant, uncompensated minority charge carriers on the Fe<sub>B</sub> sublattice give rise to half-metallic behavior.

Since the first spin-resolved photoemission (PE) study on the band structure of natural magnetite single crystals in the 1970s [5], there have been many further attempts to determine the spin polarization. Depending on the type of samples single crystals and thin films prepared by different deposition techniques—and, specifically, surface orientation and preparation, values for the spin polarization at the Fermi energy  $(E_F)$  ranging from +30% to -80% have been reported over the past 40 years (see Table I) [5–17].

Generally, this surprisingly large scatter of values is rooted in the fact that previous photoemission studies employed low excitation energies in the range from several 10 to several 100 eV, resulting in a rather low probing depth of a few atomic layers only. In some cases, photon energies below 10 eV were used, but due to the lack of systematic data, it is unclear whether, concomitantly, the probing depth is enhanced, as was shown for some selected materials [18,19].

A low probing depth, however, hampers the interpretation of the spin polarization data in the case of magnetite since, due to the specific stacking order of the  $Fe^{2+/3+}$  cations and  $O^{2-}$  anions in its inverse-spinel crystal structure, the surfaces are polar, which renders them highly unstable with respect to atomic reconstruction [20-22]. This in turn affects the magnetic and electronic properties at the surface, which thus may strongly deviate from those of the bulk. In fact, the intrinsic instability of the magnetite (100) and (111) surfaces is known to result in a variety of possible metastable reconstructions [23–25]. Furthermore, the corresponding phases strongly depend on the details of the surface preparation [25], which can cause poor reproducibility in experiment. It is thus not surprising that photoemission has provided a broad range of spin polarization values, with a reliable experimental determination of the true intrinsic bulk value still lacking.

From a theoretical point of view, density-functional theory (DFT) calculations indicate a complete bulk spin polarization of -100% at  $E_F$  [16,23,24,26–53]. We note that the few studies explicitly accounting for surface effects [23,41] find the electrons at  $E_F$  only partially polarized, highlighting again that the properties of surface and bulk strongly differ in magnetite. However, one should bear in mind that the electronic and magnetic properties of magnetite, exhibiting a correlation-induced phase transition, the so-called Verwey transition, may not be adequately captured by DFT calculations since correlations are treated only statically on a mean-field level. Furthermore, only ground-state properties

Authors	Sample Method of sample/surface preparation		Photon energy (eV)	$P$ at $E_F$ (%)	
Kay et al. [6]	$Fe_3O_4(n/a)$	reactive sputter deposition on quartz	4.5	+30	
Kim et al. [7]	$Fe_3O_4(111)$	oxidation of Fe films grown on W(110)	40	+16	
Alvarado <i>et al.</i> [5]	Fe <sub>3</sub> O <sub>4</sub> nsc	cleaved single crystal	4.5	-35	
Morton et al. [8]	Fe <sub>3</sub> O <sub>4</sub> (100)	reactive DC sputtering	160	-40	
Vescovo et al. [9]	Fe <sub>3</sub> O <sub>4</sub> (100)	plasma-assisted MBE	40	-50	
Fonin <i>et al.</i> [10–12]	$Fe_3O_4(100)$	MBE	58	-55	
Huang <i>et al.</i> [13]	$Fe_3O_4(100)$	MBE	450	-55.5	
Alvarado et al. [14]	Fe <sub>3</sub> O <sub>4</sub> nsc	cleaved single crystal	5.2	-65	
Tobin <i>et al.</i> [15]	$Fe_3O_4(100)$	reactive DC sputtering	160	-65	
Wang <i>et al.</i> [16]	$Fe_3O_4(100)$	epitaxial grown on MgO(001)	4.65	-72	
Dedkov et al. [17]	$Fe_3O_4(111)$	oxidation of Fe films grown on W(110)	21.2	-80	
Fonin <i>et al.</i> [10,12]	Fe <sub>3</sub> O <sub>4</sub> (111)	oxidation of Fe films grown on W(110)	21.2	-80	

TABLE I.	Overview of the mea	sured spin polarizations H	<sup>p</sup> from previous	spin-resolved	photoemission	studies. (I	DC denotes	direct of	urrent,
MBE denotes	molecular beam epita	xy, and nsc denotes natur	al single crystal	.)					

are considered in DFT instead of the photoemission process itself. Alvarado and Bagus [54] early on did consider the actual photoemission process in a single ion model for ferrites, accounting for the spin coupling between the photoelectron and the final state of the correlated  $3d^{n-1}$ -shell left behind. This approach, describing the atomic limit, also results in a negative spin polarization with the emission predominantly that of minority spin electrons, due to the high-spin final state for more than half-filled 3d shells, but with a significantly lower value of -66.7%. Clearly, this model completely neglects band-structure effects. An overview of previous theoretical studies and the predicted spin polarizations *P* therein is shown in Table II.

To settle the issue of the intrinsic spin polarization of magnetite, truly bulk-sensitive spin-resolved PE has to be performed to rule out any surface effects. Previous spin- and angle-integrated measurements of the valence band showed still significant differences in the spectra for the (111) and (100) surface orientations at photon energies as high as  $\approx$ 700 eV [55]. Therefore, to really probe bulk properties, photon energies in the hard x-ray regime have to be used. This was previously hampered by the notoriously low photoionization cross sections in the hard x-ray regime in combination with the poor efficiency for Mott scattering, which for a long time was the basic design principle of photoemission spin detectors. Therefore, new routes have to be followed [56–59] to enable bulk-sensitive, spin-resolved photoemission experiments. In our study, this was accomplished by using a newly developed time-of-flight (TOF) k-space microscopeequipped with a spin-filter crystal-that operates in the hard x-ray regime and was installed at a dedicated synchrotron beamline. Thus, this instrument allows for simultaneous energy-, spin-, and k-resolved mapping of the photoelectrons excited by each single photon pulse with unprecedented efficiency.

### II. SAMPLE GROWTH AND CHARACTERIZATION

High-quality  $Fe_3O_4(111)$  films of 30 nm thickness were grown on ZnO(0001) substrates by molecular beam epitaxy as described in Ref. [60]. Iron was evaporated from a hightemperature effusion cell in an oxygen atmosphere of about  $(3.5 \times 10^{-6})$ - $(7.0 \times 10^{-7})$  mbar while the substrate was kept at a temperature of 400°C. These growth parameters are crucial since there are many stable iron oxide compounds beside magnetite [61].

In a previous study, we have already shown by measuring with a superconducting quantum interference device (SQUID) that our magnetite films show a spin-reorientation transition at 128 K, which is known to lie approximately 10 K above the actual Verwey transition temperature and is comparable to those observed in bulk single crystals [60]. Furthermore, x-ray diffraction (XRD)  $\omega$ -2 $\theta$  scans and rocking curves exhibit nearly completely relaxed growth on ZnO and single-crystal quality, as indicated by a full width at half-maximum of the rocking curves of only  $0.04^{\circ}$  [60,62].

To further check the crystalline quality of the films, *in situ* low-energy electron diffraction (LEED) was performed [see Fig. 1(a)]. The sharp hexagonal  $2 \times 2$  LEED pattern, showing the reciprocal primitive cells of the oxygen (red) and iron (blue) sublattices, confirms the formation of an atomically long-range-ordered Fe<sub>3</sub>O<sub>4</sub>(111) surface [63].

A big advantage of the TOF *k*-space microscope used in this study (see the Appendix) is its capability to acquire constant energy maps "at one shot," i.e., without tilting the sample. This provides the possibility to record hard x-ray photoelectron diffraction (hXPD) patterns with large probing depths in only a few minutes, even on samples that have been previously exposed to air. While LEED essentially yields information on the structural quality and symmetry of the very surface, hXPD, being based on the forward scattering of photoelectrons, gives detailed information about the geometrical structure of subsurface atomic layers reaching far into the bulk [64].

Figure 1(b) displays on the left side the measured hXPD patterns for the Fe 3*p* and O 2*p* core levels along with simulations on the right side, based on the many-beam dynamical theory of electron diffraction [65]. The hXPD patterns of Fe 3*p* and O 2*p* were measured with excitation energies of 5204 eV ( $E_{\rm kin} = 5150$  eV) and 5000 eV ( $E_{\rm kin} = 4993$  eV), respectively. The simulations were carried out at the same energies. The good agreement of theory and experiment confirms the good structural quality of the sample also in the bulk and supports the claim

Authors	Year	Implementation/Approximation	$P$ at $E_F$ (%)
Alvarado and Bagus [54]	1978	single ion model	-66.7 <sup>b</sup>
Yanase and Siratori [26]	1984	SC-APW	-100
de Groot and Buschow [27]	1986	GGA(SC-ASW)	-100
Zhang and Satpathy [28]	1991	LSDA(LMTO-ASA)	-100
Pénicaud <i>et al.</i> [29]	1992	GGA(SC-ASW)	-100
Anisimov <i>et al.</i> [30]	1996	LSDA	-100
Yanase and Hamada [31]	1999	FP-APW	-100
Antonov <i>et al.</i> [32,33]	2001, 2003	LSDA+U	-100
Jeng <i>et al.</i> [34–36]	2002, 2004, 2006	LSDA(APW, ASW, LMTO)/LDA+U	-100
Szotek <i>et al.</i> [37]	2003	SIC-LSDA	-100
Leonov <i>et al.</i> [38]	2004	LSDA+U(TBLMTO)	-100
Madsen and Novák [39]	2005	LDA+U(FLL-DCC)	-100
Pentcheva <i>et al.</i> [23]	2005	GGA(FP-APW)	$-40^{a}$
Pinto and Elliott [40]	2006	GGA+U(PAW)	-100
Zhu <i>et al.</i> [24]	2006	LDA+U	-100
Łodziana [41]	2007	GGA+U	$> -100^{a}$
Piekarz <i>et al.</i> [42,43]	2007, 2010	GGA(+U)	-100
Rowan <i>et al.</i> [44]	2009	GGA	-100
Yu <i>et al.</i> [45]	2012	GGA+U	-100
Arras et al. [46]	2013	LSDA+U(FP-APW)	-100
Wang <i>et al.</i> [16]	2013	GGA+U	-100
Noh <i>et al.</i> [47]	2014	GGA+U	-100
Schmitz <i>et al.</i> [48]	2014	GGA+U	-100
Liu et al. [49,50]	2017, 2019	GGA+U/SCC-DFTB	-100
Mounkachi et al. [51]	2017	SIC-LSDA	-100
Chen <i>et al.</i> [52]	2018	GGA(+U)	-100
Sai Gautam and Carter [53]	2018	SCAN(+U)(PAW)	-100

TABLE II.	Theoretical	calculations	based or	various	approximat	ions and	their r	predicted	bulk s	pin 1	polariz	ation I	Ρ.

SC/FP-APW: Self-consistent/full-potential augmented-plane-wave, SC-ASW: Self-consistent augmented spherical waves, FLL-DCC: Fully localized limit - double counting corrected, GGA: Generalized gradient approximation, (TB)LMTO(-ASA): (Tight binding) linear muffin-tin orbital (atomic spheres approximation), PAW: Projector augmented wave, (SIC)-L(S)DA: (Self-interaction corrected) local (spin) density approximation, SCAN: Strongly constrained and appropriately normed, SCC-DFTB: Self-consistent charge density functional tight binding. <sup>a</sup>Calculations were done explicitly for the surface of  $Fe_3O_4(001)$ .

<sup>b</sup>Represents the photoelectron spin polarization of the whole  $Fe^{2+} 3d$  shell.



FIG. 1. (a) LEED pattern (98.5 eV) of a freshly grown magnetite film, showing the reciprocal primitive cells of the oxygen (red) and iron (blue) sublattices. (b) hXPD patterns of the Fe 3p ( $E_{\rm kin} =$ 5150 eV) and O 2p ( $E_{\rm kin} = 4993$  eV) core levels: experimental data on the left and calculated diffraction patterns on the right are in good agreement, confirming the excellent structural quality of the film and also supporting the claim of bulk sensitivity of the measurements. The hXPD patterns cover an angle range of  $\pm 9^{\circ}$ .

of a truly bulk-sensitive measurement at these photon energies.

In addition, immediately after epitaxial growth within the same vacuum system, XPS using Al  $K\alpha$  radiation and an Omicron EA 125 hemispherical deflection analyzer (HDA) was performed in our home laboratory in Würzburg. In Fig. 2(a) the Fe 2p core level spectrum is shown, exhibiting the characteristic line shape of magnetite as originates from the Fe<sup>2+</sup> and Fe<sup>3+</sup> ions of this mixed-valency compound including corresponding charge-transfer (CT) satellites, and it is markedly distinct from other iron oxides [61]. In (b) the XPS spectrum of the valence band is compared to an ex situ spin-integrated photoemission spectrum of the same sample recorded with the TOF microscope at the hard x-ray beamline P22 at the synchrotron PETRA III, DESY (Hamburg, Germany) [66]. Due to the better energy resolution of the TOF instrument in combination with the highly brilliant synchrotron radiation, the Fe 3d states at  $E_F$  are less broadened and hence appear more pronounced than in the spectrum taken in our home laboratory. Otherwise, the different spectral line shapes can be explained by the relative change in the photoionization cross sections of the O 2p and Fe 3d states that are hybridized with each other. Nevertheless, for both photon energies the



FIG. 2. (a) Fe 2p core-level spectrum measured with Al  $K\alpha$  radiation, showing Fe<sup>2+</sup> and Fe<sup>3+</sup> contributions due to the mixed valency of magnetite as well as charge-transfer (CT) satellites. (b) Hard x-ray (blue) and laboratory-based (red) valence-band spectra of the same magnetite film. The Fe 3*d* states at  $E_F$  are clearly distinguishable from the O 2p valence band.

predominant contribution of the Fe 3d states at the Fermi level remains clearly distinguishable from the mainly O 2p-derived valence-band spectral weight at higher binding energies.

Furthermore, x-ray magnetic circular dichroism (XMCD) has been measured on an LN<sub>2</sub> cooled film in total electron yield mode at the TEMPO beamline (SOLEIL, France) to establish magnetic ordering. The blue and red spectra in Fig. 3 reflect the absorption measured at the Fe  $L_{2,3}$  edge ( $2p \rightarrow 3d$ transition) with different helicity (parallel  $\sigma_+$  and antiparallel  $\sigma_{-}$  with respect to the in-plane magnetization). Both curves were normalized by the mirror current  $I_0$ , which is a measure for the incident photon flux. The absorption spectra and the resulting XMCD signal  $[(\sigma_+ - \sigma_-) \times 2, \text{ corrected for the}$ experimental geometry with the beam incidence under 45° relative to the surface normal], which is shown as a green dashed line in Fig. 3 [67], are in very good agreement with other theoretical and experimental studies on magnetite thin films [68–72]. The three peaks in the XMCD signal thereby represent the B-site Fe ions [(a) and (c)] and the Fe<sup>3+</sup> ions on the A-site [(b)].

To summarize this section, SQUID and XRD measurements from a previous study as well as LEED, hXPD, spin-integrated photoemission, and XMCD establish the high



FIG. 3. X-ray magnetic circular dichroism measured at the Fe  $L_{2,3}$  absorption edge. The blue and red curves reflect the absorption for different helicity  $\sigma_+$  and  $\sigma_-$ , respectively. Both curves were normalized by the mirror current  $I_0$ . The resulting XMCD signal is shown as a green dashed line (multiplied by 2).

quality of the  $Fe_3O_4$  films in terms of bulk and surface crystallinity, magnetic ordering, and stoichiometric composition. They hence can be regarded as representative for bulk properties similar to single crystals.

#### **III. SPIN-RESOLVED PHOTOEMISSION**

In our photoemission experiment, we use the spindependent reflectivity at the surface of an iridium single crystal to gain information on the photoelectron spin (see the Appendix and references therein for detailed information). The strongest spin-sensitivity is achieved if the photoelectrons are decelerated to a kinetic energy of about 12.5 eV when impinging on the spin-filter crystal, making the spin-dependent scattering extremely surface-sensitive. Therefore, prior to the spin-resolved measurements, the surface of the iridium spinfilter crystal was freshly prepared by several high-temperature flashes in an oxygen atmosphere to get rid of surface contaminants such as carbon and nitrogen compounds, which can significantly decrease the reflectivity and spin asymmetry of the reflected intensity [73]. The low scattering energy concentrates all reflected intensity into only a few diffraction spots, being favorable for the figure-of-merit of spin detection using the specular (0,0) reflex.

Although the microscope allows for simultaneous spinand *k*-resolved mapping of the photoelectrons, due to the weak dispersion of the Fe 3*d* bands, their momentum dependence cannot be resolved [74]. Therefore, the spin-resolved data will be integrated over the area covered by the spin-filter crystal ( $\approx 7 \text{ Å}^{-1}$  in the  $k_x$ -direction and  $\approx 4 \text{ Å}^{-1}$  in the  $k_y$ -direction), granting a higher signal-to-noise ratio due to higher count rates. The sample was cooled down to a temperature of  $\approx 30 \text{ K}$ in order to avoid magnetic fluctuations and—as a positive side effect—to reduce the Debye-Waller factor that determines the strength of direct transitions in relation to phonon-induced thermal scattering contributions. The cooled sample was then magnetized in-plane ( $I^+$ ) with a permanent magnet. The



FIG. 4. (a) Valence-band spectra measured with an excitation energy of  $h\nu = 5.0$  keV for two opposite in-plane magnetizations denoted by  $I^+$  and  $I^-$ . (b) Energy-dependent asymmetry A, calculated with Eq. (1).

applied field amounted to 1 T parallel to the film and to the quantization axis of the spin detector, large enough to drive the sample into saturation. The valence band was then measured in remanence with an excitation energy of hv = 5.0 keV [75], leading to a photoelectron inelastic mean free path of  $\approx 70$  Å [76] and an energy resolution of  $\approx 620$  meV—using a Si(111) monochromator crystal pair for maximum photon flux. Then the sample was magnetized in the opposite direction ( $I^-$ ) and measured again. Figure 4(a) shows the spectra for the two opposite in-plane magnetization directions for the relevant energy range from  $E_F$  up to 5 eV. The inset shows the entire acquired range up to 10 eV with no visible difference in the spectral shape for binding energies above 3 eV.

In contrast, clear differences between the two magnetizations are seen for smaller binding energies. The resulting intensity asymmetry A, defined by

$$A = \frac{I^+ - I^-}{I^+ + I^-},\tag{1}$$

is plotted in Fig. 4(b). It is zero above 3 eV where the O 2p valence band dominates. For smaller binding energies and with predominantly Fe 3*d* states contributing, the asymmetry first becomes negative and switches sign between 0.95 and 0.60 eV with a maximum at 0.80 eV. Closer to the Fermi level, the asymmetry turns negative again and assumes a maximum negative value at  $E_F$ .

The conversion of the measured asymmetry A into an actual spin polarization P involves the Sherman function, being



FIG. 5. Energy-dependent Sherman function S(E), calibrated using the known 100% spin polarization of the Eu 4*f* states of an EuO thin film. The bottom axis refers to the actual scattering energy at the spin-filter crystal. In the top axis these values are converted to a binding energy scale, as adapted to the spin-resolved magnetite spectra of Fig. 4.

a measure of the spin-sensitivity of the used spin-filter crystal:

$$P = \frac{N^{\uparrow} - N^{\downarrow}}{N^{\uparrow} + N^{\downarrow}} = \frac{1}{S} \frac{I^{+} - I^{-}}{I^{+} + I^{-}},$$
 (2)

where  $N^{\uparrow}$  and  $N^{\downarrow}$  are the total photoelectron numbers with spin  $\uparrow$  and  $\downarrow$ , respectively. It is important to realize that in our specific experimental approach, the explicit energy de*pendence* of the Sherman function S = S(E) is required, in contrast to conventional spin-detectors operated at a fixed energy only. Employing TOF energy recording, all photoelectrons in the measured energy window are reflected off the spin-filter crystal essentially simultaneously, i.e., at different scattering energies. For the data in Fig. 4, the electron optics was set in such a way that photoelectrons originating from the maximum of the Fe 3d peak at  $\approx 0.5$  eV reach the spin-filter crystal at a kinetic energy where its Sherman function assumes its maximum ( $\approx$ 12.5 eV) [77]. Consequently, electrons at higher (lower) binding energy get scattered at lower (higher) kinetic energy, with subsequently different spin efficiency as captured by S(E) and hence necessitating a careful calibration of the Sherman function.

Such a calibration is best achieved on a material system with known spin polarization. Here we chose EuO whose Eu 4f states have been demonstrated to display a spin polarization of 100% [78,79]. Based on this value, we measured the experimental spin asymmetry of the 4f states of a thin EuO film [79] for scattering energies between 9.5 and 13.2 eV, and we calculated the associated values of the Sherman function. Figure 5 depicts the corresponding data points together with a spline interpolation. The Sherman function assumes its maximum around 12.5 eV, while at lower kinetic energies, i.e., higher binding energies, S(E) is significantly decreasing and even changes its sign at about 10.9 eV.

Based on this calibration of the Sherman function, we finally determine the energy-dependent spin polarization P(E)



FIG. 6. Spin polarization of the magnetite film, calculated with Eq. (2) (the line serves as a guide to the eye). It is negative at  $E_F = 0$  eV with a value of -80%. Between 0.60 and 0.95 eV, there is a sign change of the polarization. The error bars denote the statistical error.

of our magnetite film from Eq. (2). The result is shown in Fig. 6. As predicted by theory, the spin polarization at  $E_F$  is negative. With higher binding energies, the absolute value of the spin polarization decreases and switches sign at 0.60 eV. It exhibits a maximum with further increasing binding energies and becomes negative again at 0.95 eV. Since the Sherman function has a zero at about 10.9 eV, corresponding to a binding energy of 2.1 eV in our study, the spin polarization unphysically diverges around this energy, and hence we focus in Fig. 6 on smaller binding energies from 1.2 eV up to the Fermi level, where the Sherman function does not vary strongly and the polarization is not affected by the zero in *S*. For binding energies above 3 eV, the polarization becomes zero (see Fig. 4).

To give a quantitative estimate of the spin polarization at  $E_F$  from the measured asymmetry, we first point out that the measurements were performed at  $\approx 30$  K, i.e., below the Verwey temperature, at which a metal-insulator transition takes place and a small gap of about 50 meV with respect to  $E_F$  opens [55]. So, strictly speaking, there are no states at  $E_F$  and thus no defined spin polarization. However, the finite energy resolution of about 600 meV in our experiment transfers detectable spectral weight to the Fermi level, resulting in a finite polarization signal. The experimental spin polarization at the Fermi level  $P(E_F)$  can now be determined from Fig. 6 to be -80% (dashed green line).

The statistical error for the asymmetry shown in Fig. 4(b) is estimated from the count rates  $I^+$  and  $I^-$  in a 50 meV energy interval near  $E_F$  for both magnetization directions,  $\Delta A = \sqrt{4I^+I^-/I^3} = 0.012$  (with  $I = I^+ + I^-$ ). The statistical error of the Sherman function related to the calibration measurement is in the same order of magnitude,  $\Delta S = 0.013$  (see Fig. 5). The statistical error of the polarization value results from the sum of the relative errors,  $\Delta P/P = \Delta A/A + \Delta S/S$ . Near the Fermi energy, the statistical error amounts to  $\Delta P/P = 0.13$  and  $\Delta P = 0.104$ . As additional systematic errors, we take into account (i) reduced remnant magnetiza-



FIG. 7. Majority and minority spin-DOS (red and blue triangles, respectively) for Fe<sub>3</sub>O<sub>4</sub>, calculated from the results of Fig. 4 using Eq. (3) with error bars denoting the statistical error. Mostly minority spin states are located at  $E_F$ . The spin-DOS overall resembles those from DFT calculations (solid lines) in Ref. [42], especially upon convolution with the instrumental resolution (dashed lines).

tion compared to the intrinsic magnetization, and (ii) finite energy resolution. (i) As the sample was measured in remanence, the magnetization  $M_r$  and thereby the spin polarization could be lower than the intrinsic magnetization  $M_s$ . Previous SQUID magnetometry on similarly prepared samples results in  $M_r/M_s = 0.64$  [60]. Therefore, the intrinsic spin polarization could be larger than the measured value. (ii) Due to the specific shape of the energy-dependent polarization data in Fig. 6 (with a maximal positive spin polarization at 0.8 eV, a sign change at 0.6 eV, and a maximal negative spin polarization at the Fermi energy), a finite-energy resolution tends to reduce the measured spin polarization at  $E_F$ . Therefore, the measured spin polarization at  $E_F$  represents a *lower limit* of its true absolute value and strongly points to a full spin polarization at  $E_F$  of -100%, supporting the assumption of magnetite being a half-metallic ferromagnet. Considering both statistical and systematical errors, the spin polarization value at  $E_F$  amounts to  $P(E_F) = -80^{+10}_{-20}\%$ .

Finally, the spin-resolved density of states (spin-DOS) can be inferred from Eq. (2) with  $N_{\text{tot}} = N^{\uparrow} + N^{\downarrow}$ :

$$N^{\uparrow\downarrow} = \frac{1}{2}(1\pm P)N_{\text{tot}}.$$
(3)

The resulting majority and minority spin-densities are shown in Fig. 7 (red and blue triangles). Also shown are the results of DFT calculations by Piekarz *et al.* [42]—performed explicitly for the low-temperature phase of magnetite with the monoclinic P2/c symmetry [80,81] and including strong correlation effects on the GGA+U level—without (solid lines) and with (dashed lines) the experimental broadening taken into account. While the experimental spin-densities overall resemble the theoretical ones, there are also notable quantitative differences. It has been argued that, in general, magnetite should be considered a correlated electron system, casting a description by DFT and its findings of half-metallicity into doubt [13]. Furthermore, the excitation of spin waves [10,17,82,83] and the formation of polarons [16], which both are not captured by DFT calculations, were put forward in previous experimental studies to explain a smaller spin polarization observed in experiment than predicted by DFT. Such effects also will affect the detailed experimental line shapes in the near- $E_F$  region.

### **IV. CONCLUSIONS**

In this study, we have measured the bulk spin polarization of magnetite by spin-resolved photoelectron spectroscopy. For these experiments, we have utilized a new generation of photoemission instrumentation. It features time-of-flight energy recording in combination with imaging spin-filtering, and it is adapted for operation with hard x-rays at a dedicated synchrotron beamline to strongly enhance the probing depth. With this setup, it has become possible to overcome the notorious problem of ill-defined magnetite surfaces from which previous low-energy spin-resolved photoemission studies suffered. The measured spin polarization of  $-80^{+10}_{-20}\%$  strongly points to a full bulk spin polarization at  $E_F$ , fully compatible with theoretical predictions from density-functional theory that magnetite is a half-metallic ferromagnet.

From an experimental view, further advancements in instrumentation, regarding both electron and photon energy resolution, will make it possible to narrow down the experimental uncertainty for the spin polarization of magnetite further [84]. This will have to be matched by improved theoretical approaches, taking properly into account both the itinerancy of the minority charge carriers at the Fermi energy as well as their correlations and coupling to the lattice degrees of freedom. Nevertheless, our present results point to a full bulk spin polarization near  $E_F$  that originates from spin-down charge carriers, and thereby they provide strong experimental support to the theoretical view of magnetite as a half-metallic ferromagnet.

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FIG. 8. Design (side view) and principal operation of the newly set up microscope at beamline P22, DESY. Notice that the spin-filter also preserves the energy information encoded in the time-of-flight signal (see the inset), resulting in a 3D ( $k_x$ ,  $k_y$ ,  $E_{kin}$ ) recording scheme.

### APPENDIX: SPIN-RESOLVED TIME-OF-FLIGHT k-SPACE MICROSCOPY

Spin-resolved photoemission poses very high demands on the experimental setup since the discrimination of spin orientations, on whichever microscopic mechanism it is based, in general has a very low efficiency compared to spin-integrated photoemission. Hence, it is important to generate and count as many photoelectrons as possible. One of the most common setups to date is the combination of a hemispherical deflection analyzer (HDA) with a Mott detector [85]. However, due to the tremendous decrease of the photoabsorption cross sections with increasing photon energies, such instruments are of limited use in the hard x-ray regime-especially when studying valence bands—since they only offer single-channel detection. To benefit from the multichannel capabilities of modern energy analyzers and detectors, a new type of spin detector-known from the soft x-ray and vacuum ultraviolet (VUV) spectral range [77,86]-was adopted for hard x-rays several years ago, making use of an iridium single crystal as a spin-filter [77]. Although the reflectivity of the spin-filter crystal is in the range of only a few percent, the spin-resolved, parallel acquisition of photoelectrons makes such instruments superior to spectrometers equipped with a Mott detector.

As a further improvement—instead of employing the 2D recording scheme of a HDA, which requires entrance and exit slits to obtain a decent energy resolution at the sacrifice of electron count rates-the TOF method was introduced to discriminate all electrons emitted from a single photon pulse with respect to their energy enabling 3D ( $k_x$ ,  $k_y$ ,  $E_{kin}$ ) recording, and thus it profits from much higher count rates. Based on this technique combined with a newly designed extractor lens, optimized for low aberrations at very high excitation energies, a highly efficient k- and spin-resolved TOF microscope was set up at P22, DESY (Hamburg, Germany) [66]. A sketch of the principal components is illustrated in Fig. 8. The spinfilter crystal is retractable, allowing for two branches-each with its own delay-line detector. One for measuring spin- and k-resolved with a scattering angle of  $56^{\circ}$  with respect to the crystal surface normal, and the other one for high-intensity spin-integrated k-mapping. Using the 40-bunch mode of PE-TRA III with a bunch separation of 192 ns, the energy and momentum resolution of the microscope for the measurements shown here amounted to 40 meV and 0.025 Å<sup>-1</sup>, respectively, which represent typical values for this kind of instrument [87,88]. The key factor making the present experiment feasible is the increased figure-of-merit of the spin-filter approach shown in the inset. A comparison of quantitative values for different spin-filter concepts is given in Fig. 28 of Ref. [89].

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